

Short communication

Improved, high conductivity titanium sub-oxide coated electrodes obtained by Atmospheric Plasma Spray



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HIGHLIGHTS

- Titanium sub-oxide coatings were obtained by Atmospheric Plasma Spray.
- Coated samples exhibited good mechanical properties.
- Coated samples showed an increased range of operation than uncoated electrodes.
- Coated samples had higher electrical conductivity compared to standard electrodes.

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ABSTRACT

Coatings based on reduced stoichiometries of titanium dioxide obtained by Atmospheric Plasma Spray are presented for their application as electrodes in devices such as lead acid batteries, redox flow batteries and electrochemical reactors. A study of their microstructure, composition and mechanical properties is first presented in this paper to show that the layers are compact, free of cracking and well adhered to the substrate. The presence of Magnéli phase oxides, particularly Ti_8O_{15} was identified in the coatings, which enhances their electrical conductivity. In order to understand the behaviour of this material as an electrode, an electrochemical analysis of the coatings was also done. The coated samples showed higher oxygen and hydrogen evolution overpotentials and lower electrochemical corrosion compared to typically used commercial stainless steel and carbon–polymer composite electrodes.

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1. Introduction

Bipolar lead acid batteries have attracted attention because of potential improvements in active mass utilization, uniform current distribution and lighter-weight construction (higher energy density) in comparison to conventional batteries that contain lead grids [1]. Furthermore, bipolar electrodes are typically used for redox flow batteries, fuel cells and electrochemical reactors. In these electrochemical devices, a stack of bipoles are arranged such that the current passes orthogonally and the stack is capped by two endplates (monopoles). Bipolar electrodes for such applications must be electrically conductive but chemically inert; the operating environment is often highly acidic or alkali and highly positive and

negative electrode potentials are desirable. Currently the material of choice is often carbon or carbon composites. These can suffer from degradation over time and are limited in electrical conductivity. Metallic plates have considerably higher electrical conductivity, are lower cost and easier to manufacture but are not stable in the electrolytes or at the operational potentials required. If low cost metallic substrates could be coated with an electrically conductive, chemically robust layer, they would have significant commercial potential. From a cost-effectiveness point of view, processes that can provide the active components in these devices like electrodes, bipolar walls or even insulating layers in a rapid manufacturing process would be highly beneficial. Thermal spray technologies provide a very interesting solution that can fit in this necessity. Atmospheric Plasma Spray (APS) builds-up coatings by the impact onto a substrate of powder particles that are propelled by a plasma jet, which is formed via a typical gaseous mixture of Ar/H_2 that flows through an electric arc [2]. APS has been extensively used for

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producing passive surfaces that work against wear and corrosion phenomena. Nevertheless, it is also possible to develop functional active surfaces by this technique [3].

In this paper, titanium sub-oxide (TiO_{2-x}) coatings obtained by APS onto stainless steel substrates are presented as low cost, chemically inert electrodes principally for batteries but also potentially for many aqueous electrochemical devices. Optimized spraying conditions starting from previous studies have been selected and the mechanical properties of the obtained samples are included. The electrochemical characterization of the thermal spray coatings has been also carried out with the aim of forecasting its performance as electrodes and the results were compared with commercial standard materials.

2. Experimental

A feedstock powder based on rutile TiO_2 and Magnéli phases (Ti_8O_{15} and Ti_9O_{17}) was sprayed using an APS A-3000S system with an F4 plasma torch (Sulzer Metco, Germany). The particle size distribution was measured by Laser Scattering using the LS Beckman Coulter equipment. Powder and cross-section area of the coatings was studied by Scanning Electron Microscopy, SEM (JSM-5310, Jeol). The phase composition powder and coating was analyzed by a X'Pert PRO MPD diffractometer (PANalytical). Coated samples were cut and mounted in a conductive phenolic resin (Konductomet, Buehler) followed by the metallographic preparation. The hardness of the coatings was analyzed by a MXT- α microhardness tester (Matsuzawa) following the UNE 7-423/2 standard. In order to determine the bonding strengths of the sprayed samples, adhesion tests were performed on each selected coating following the ASTM F1147 (2005) standard. A testing apparatus SERVOSIS ME-402/10 model was used with a cross-head velocity of 0.02 mm s^{-1} , which was controlled by under displacement. Electrolytes for electrochemical characterization of the electrodes were made using deionized water obtained from a Purite water purifier. KOH and H_2SO_4 were used as received from Sigma Aldrich. Electrochemical measurements were taken in a standard two-compartment glass electrochemical cell using an Autolab potentiostat/galvanostat operating with GPES acquisition software. Potentials were measured against a saturated calomel reference electrode (SCE) and a platinum counter electrode was used. Measurements were taken at 20°C electrolytes were de-oxygenated using a vigorous stream of N_2 gas.

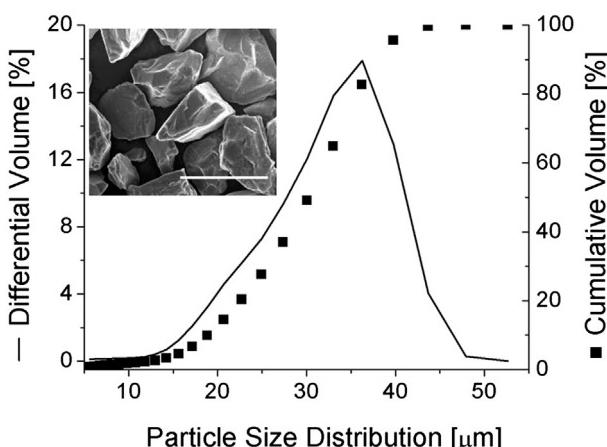


Fig. 1. Particle size distribution of the sprayed powder. A scanning electron micrograph of the feedstock (the scale bar represents 50 microns) is also given.

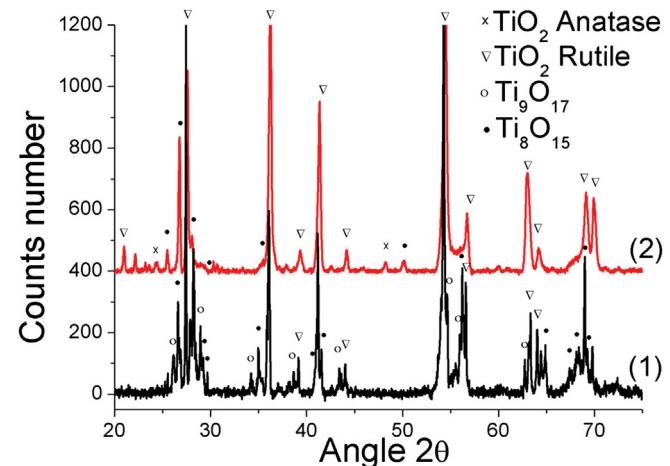


Fig. 2. Comparison between the XRD of the starting powder (1) and the obtained coating (2).

3. Results and discussion

The spraying conditions were optimized in a previous work, which focused on arc current intensity, stand-off distance and the influence of H_2 in the plasma power [4]. A strong correlation between particle temperature and the number of cracks in the coating cross-section was found. The particle size distribution of the powder and a micrograph can be observed in Fig. 1. The feed rate of the powder into the plasma jet and especially the gun velocity were also varied leading finally to a sample with a resistivity of $0.05 \Omega \text{ cm}$. Fig. 2 shows the X-Ray Diffraction (XRD) analysis of the feedstock powder and the optimized coating. A certain loss of the percentage of Magnéli phases was found when spraying the powder. A low flow rate of hydrogen was used in these spraying conditions in order to decrease the temperature of the particles due to hydrogen plasma has a higher heat convection coefficient. However, it was noted that lower rates of hydrogen and higher rates of argon may partially re-oxidize the reduced stoichiometries towards titanium dioxide. Although XRD analysis of the coating shows mainly titanium dioxide in its rutile phase, it may be a lack of information related to the oxygen vacancies, which are the responsible for the electric conductivity. P.C.S. Hayfield reported the

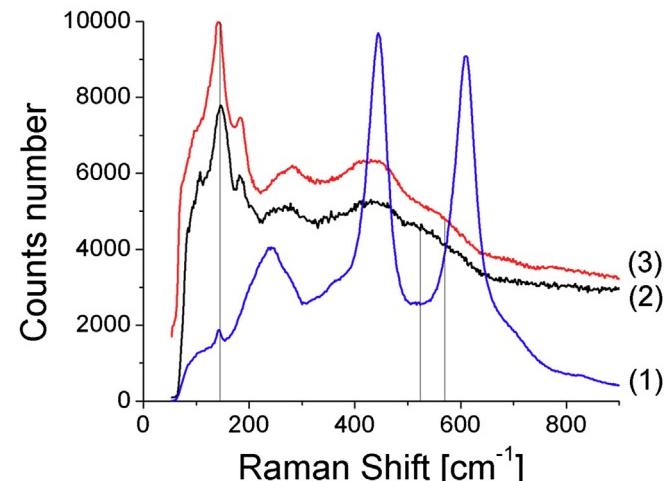


Fig. 3. Raman spectroscopy of a commercially available rutile powder (1), the feedstock powder (2) and the APS coating (3).

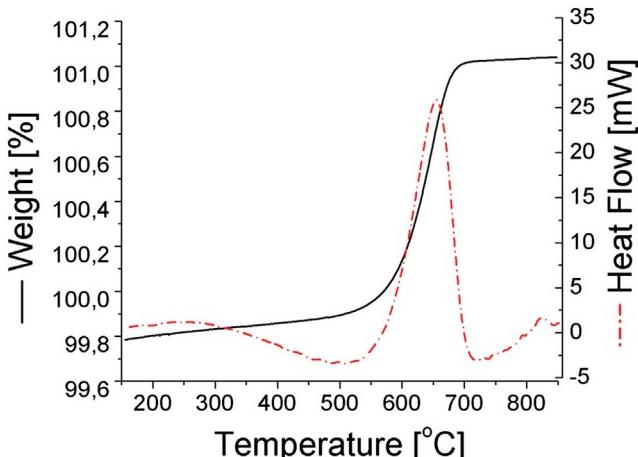


Fig. 4. DSC of the starting powder.

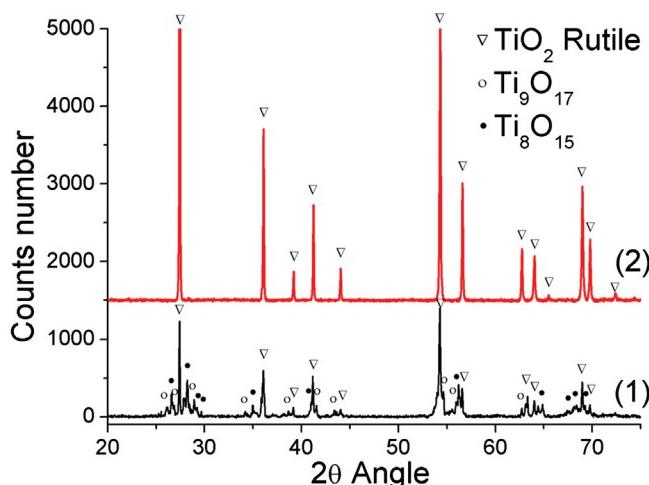


Fig. 5. Comparison between the XRD of the starting powder (1) and heated powder up to a complete oxidation (2).

overlapping of rutile XRD peaks with reduced stoichiometries of titanium oxide [5]. Raman spectroscopy can supply more information about the nature of titanium sub-oxide in its surface. It is possible to observe in Fig. 3 a comparison between the Raman spectra of a commercially available rutile powder, the feedstock powder used in this experiments and a typical spectrum of the obtained coating. As L.M. Berger et al. found previously [6], below 200 cm^{-1} the intensities of Raman peaks are attributed to reduced stoichiometries of titanium dioxide, which are not so visible for commercial rutile powder. The flattened peak above 550 cm^{-1} has been shifted to a higher wavelength when comparing the powder with the coating. This may indicate a higher amount of oxygen in the coating because of the thermal spray process.

The conductor behaviour of titanium sub-oxides is based in the existence of oxygen vacancies. A Differential Scanning Calorimetry (DSC) analysis was carried out in order to quantify the limit of the operation temperature when the coating is applied as an electrode (Fig. 4). At $500\text{ }^{\circ}\text{C}$ an exothermic peak is found, which is characteristic of an oxidation. There is also an increase of the weight due to the complete oxidation from titanium sub-oxides towards titanium dioxide, especially in oxygen-containing surroundings. Therefore, this material should not be processed in conditions above $500\text{ }^{\circ}\text{C}$ or its stoichiometry will change. This is corroborated by the XRD of the powder before and after the calorimetry (Fig. 5).

With the aim of studying the influence of the thickness in the mechanical and electrochemical properties of the samples, the number of spraying cycles was varied to obtain the following thickness: 47 μm (C146), 97 μm (C147), 155 μm (C148), 202 μm (C149) and 256 μm (C150). Fig. 6 shows SEM micrographs of the cross-section area. It is possible to observe some sub-surface porosity, typical of APS coatings, but which does not contain inter-pore linkage and so the overall coating is non-porous. The samples had a good adherence and no cracks were found in their cross-section area.

The long-term performance of an electrode in a device will be determined by a combination of its mechanical properties and chemical properties. Vickers hardness and bonding strength of the coatings were assessed as a measure of the mechanical properties. The hardness measured increases when the coating thickness is greater (Fig. 7). This suggests that the hardness measured for thin coatings is affected by the mounting resin and the substrate. This effect is reduced as coating thickness increases and therefore leads to an increase of microhardness value. As regards the tensile strength, the glue used in the test has a strength of approximately 57 MPa. The coating with lowest thickness has a bonding strength above this value. However, with increasing coating thickness a decrease to approximately 40 MPa was found. For samples C147 and C148 a cohesive rupture was observed, which implies some delamination between layers due to the increase in the number of cycles. In the case of the samples C149 and C150 an adhesive rupture was obtained and this could be due to a lower adhesion of the coating. Increasing the number of cycles (coating thickness) could boost the residual stress in the coating-substrate system which would favour decohesion between substrate and coating.

After observing the cross-section area and analyzing the mechanical properties of the different coatings, spraying conditions were selected to prepare sample C148 for building-up the TiO_{2-x} coatings and studying the electrochemical performance. Fig. 8 shows the cyclic voltammograms obtained at the APS TiO_{2-x} stainless steel coated electrode and at an uncoated stainless steel electrode. Experiments were performed at $20\text{ }^{\circ}\text{C}$ in an aqueous electrolyte solution contained 4.0 mol dm^{-3} KOH with a potential sweep rate of 50 mV s^{-1} . The uncoated stainless steel electrodes show a significant oxidation at potentials more positive than 0.5 V vs. SCE. Hydrogen evolution occurs at potentials more negative than -1.5 V vs. SCE. At the TiO_{2-x} coated electrode, an irreversible oxidation peak at circa 0.75 V vs. SCE following which, oxygen evolution occurs at potentials more positive than 1.0 V vs. SCE.

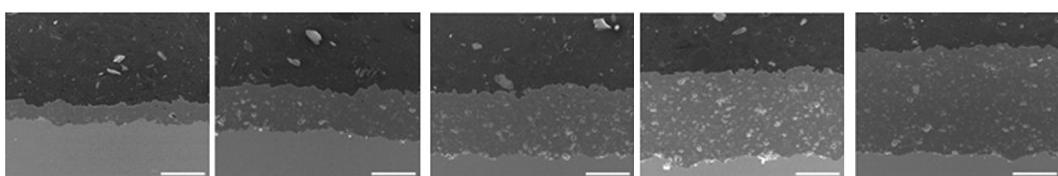


Fig. 6. Comparison of the increasing thickness of each sample by scanning electron microscopy. From left to right: C146, C147, C148, C149 and C150 (the scale bar represents $100\text{ }\mu\text{m}$).

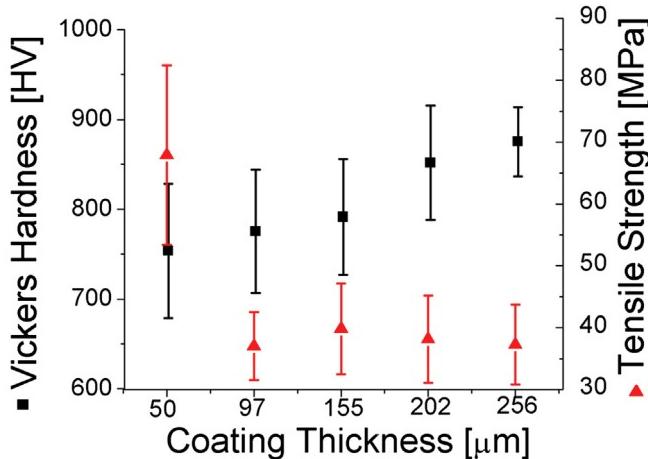


Fig. 7. Vickers hardness and tensile strength values as a function of coating thicknesses.

At negative potentials, there is also a semi-reversible reduction wave at -1.0 V vs. SCE with hydrogen evolution at potentials more negative than -1.5 V. This electrochemical response is typical of the Magnéti phase components of the coating.

A similar set of cyclic voltammograms was recorded at the coated sample and at an uncoated stainless steel substrate using an aqueous electrolyte solution contained 1.0 mol dm^{-3} H_2SO_4 . The temperature was again 20 °C with a potential sweep rate of 50 mV s^{-1} . Fig. 9 shows the obtained results. In acid media, there is also significant oxidation of the stainless steel samples at potentials higher than 1.0 V vs. SCE. Hydrogen evolution occurs at potentials more negative than -0.75 V. In contrast, the coated sample exhibits little electrochemical activity at positive potentials before the onset of oxygen evolution at circa 2.4 V vs. SCE. At negative potentials, there are a number of redox processes between 0 and -1.0 V vs. SCE with hydrogen evolution at potentials more negative than -1.0 V.

In acid and alkali environments, the overpotentials for oxygen and hydrogen evolution are larger for the coated electrodes than for the substrate stainless steel. This provides the coated electrodes of a wider potential operation window. In particular, the coating significantly suppresses the oxidation and bulk oxygen evolution of the stainless steel at positive potentials.

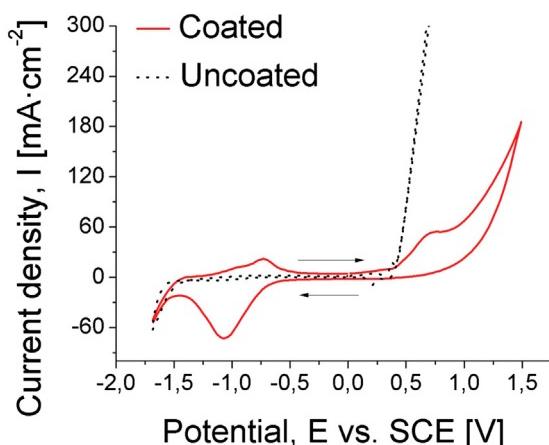


Fig. 8. Cyclic voltammograms obtained in an aqueous electrolyte solution 4.0 mol dm^{-3} KOH . APS TiO_{2-x} onto stainless steel electrode (lines) compared to uncoated stainless steel substrate (dots).

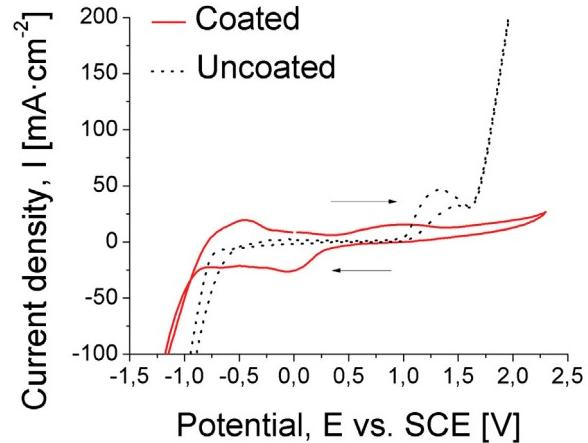


Fig. 9. Cyclic voltammograms obtained in an aqueous electrolyte solution 1.0 mol dm^{-3} H_2SO_4 . APS TiO_{2-x} coating onto stainless steel electrode (line) compared to uncoated stainless steel substrate (dots).

Additional cyclic voltammograms were also carried out and are shown in Fig. 10. In this characterization, the aqueous electrolyte solution contained 1.0 mol dm^{-3} $\text{CH}_3\text{SO}_3\text{H}$ and once again the potential sweep rate was of 50 mV s^{-1} . The stainless steel substrate exhibits hydrogen evolution commencing at approximately -0.6 V vs. SCE and oxygen evolution/corrosion commencing at approximately 1.6 V vs. SCE. In addition an anodic peak can be seen at approximately 1.2 V vs. SCE, which is probably due to oxidation of one of the stainless steel components. As in sulphuric acid, the APS TiO_{2-x} electrode demonstrates suppressed hydrogen and oxygen evolution by comparison.

Methanesulphonic acid is the electrolyte of choice for the soluble lead flow battery. In this battery, solid lead and lead dioxide deposits are plated respectively at the negative and positive electrodes during charge and then dissolved back into the electrolyte as Pb^{2+} ions during discharge. The deposition and dissolution of Pb from an aqueous electrolyte solution initially containing 1.5 mol dm^{-3} Pb^{2+} and 1.0 mol dm^{-3} $\text{CH}_3\text{SO}_3\text{H}$ was studied to show the coated stainless steel electrodes are suitable for such an application. The results of the coated samples were compared to the performance of a carbon-polymer composite electrode, typically used for the soluble lead flow battery, with equivalent dimensions (Fig. 11). The experiment

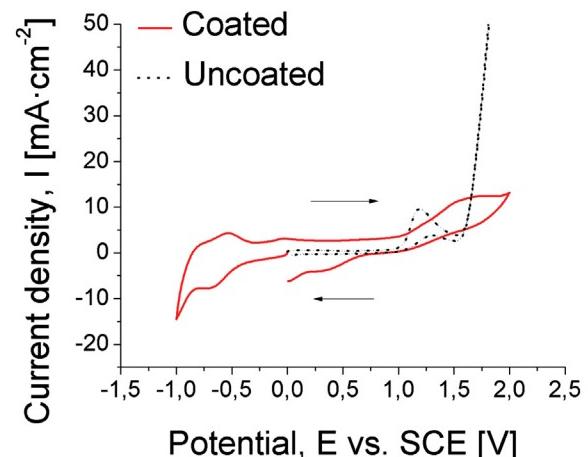


Fig. 10. Cyclic voltammograms obtained in aqueous electrolyte solution 1.0 mol dm^{-3} $\text{CH}_3\text{SO}_3\text{H}$. APS TiO_{2-x} coating onto stainless steel electrode (line) compared to uncoated stainless steel substrate (dots).

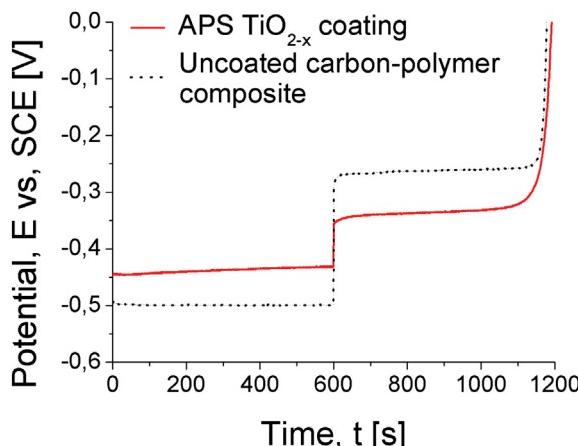


Fig. 11. Voltage vs. time plot for the deposition and dissolution of Pb from an aqueous electrolyte solution containing 1.5 mol dm^{-3} Pb^{2+} and 1.0 mol dm^{-3} $\text{CH}_3\text{SO}_3\text{H}$ (APS TiO_{2-x} coating: line, uncoated carbon composite: dots).

consisted of two periods of constant current being applied to the cell while the cell potential was monitored as a function of time. The first 600 s correspond to Pb deposition and the last 600 s correspond to Pb dissolution. The applied current density was 50 mA cm^{-2} throughout. The deposition and dissolution of Pb corresponds to the charge and discharge reactions respectively of the soluble lead acid flow battery. The lower voltage difference between deposition and dissolution reactions for the APS TiO_{2-x} electrode compared to the carbon composite are likely due to the better electrical conductivity of the former compared to the latter. Therefore, compared to the carbon–polymer electrodes, the coated ones have much better electrical conductivity and hence lower overpotential for the electrodeposition and dissolution of the electrode deposits.

4. Conclusions

Below are presented the main conclusions referred to the APS titanium sub-oxide coatings development, its mechanical properties and its suitability as electrodes:

- It is feasible to coat stainless steel with titanium sub-oxide by means of Atmospheric Plasma Spraying achieving a satisfactory electric resistivity of the coating.
- The end-use of the electrode must not exceed the 300°C in order to avoid re-oxidation of the reduced stoichiometries towards TiO_2 .
- The cross-section area of the samples showed good coating–substrate adhesion and no vertical or interlayer cracks in its cross-section area.
- As long as thickness increases, the bonding strength is decreased due to the delamination between layers and decohesion between the substrate and the coating. Moreover, the Vickers hardness increases because the influence of the resin and the substrate decreases when the samples are indented.
- In both acid and alkali environments, APS TiO_{2-x} coated samples showed an increased potential range of operation than the uncoated stainless steel electrodes.
- APS TiO_{2-x} coated samples showed a higher electrical conductivity in a simulated lead flow battery compared to the most commonly used carbon–polymer electrodes. This led to a decrease in the overpotential for the electrodeposition and dissolution in these devices. It should be noted that the coated electrodes are also likely to have a slightly higher surface area compared to the carbon composite electrodes, which would give an effectively lower current density per geometrical area but may also provide better adhesion of the deposit to the surface.

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